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(54) REFRACTORY STRUCTURE

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a refractory structure and particularly a refractory structure in sheet, paper, board, blanket, felt or cloth form or assemblies thereof suitable for heat and electric insulation, filtration, chemical treatment and acoustic insulation.

According to the invention we provide a refractory structure comprising a paper, cloth, sheet, board, blanket or felt of refractory metal oxide fibres bonded with a refractory binding agent, wherein the refractory metal oxide fibres are formed by fibrising a composition having a viscosity of greater than 1 poise comprising an aqueous solution or sol of a metal compound which can form a refractory oxide and a minor proportion of water-soluble organic polymer, drying the fibre formed and heating to decompose the nickel compound to oxide and to decompose the polymer.

If a cloth is used, it can be woven or non-woven. Alumina or zirconia fibres are very suitable for use in the invention. The refractory oxide fibre is preferably prepared by a process as described in UK Patent Specifications Nos. 1 360 197, 1 360 198, 1,360,199 and 1 360 200. In this process fibres are formed by fibrising a composition having a viscosity of greater than 1 poise comprising an aqueous solution or sol of a metal compound, for example an oxychloride, basic acetate, basic formate or nitrate of aluminium and/or zirconium, and a minor proportion of a water-soluble organic polymer, drying the fibre formed and heating to decompose the

metal compound to oxide and to decompose the polymer. Fibres only partly decomposed to oxide may be used provided that they do not dissolve in the binding composition.

Preferred water-soluble organic polymers include polyethylene oxide, polyvinyl alcohol and polyvinyl pyrrolidone.

Fibrising is preferably carried out by a blowing process, which comprises extruding the fibrising composition through one or more apertures into at least one gas stream having a component of high velocity in the direction of travel of the extruded composition. The dimensions and shape of the said aperture may vary widely. We prefer to use an aperture having at least one dimension larger than 50 microns and smaller than 500 microns. The gas stream is preferably air, more preferably air at ambient temperature. It is convenient to employ two streams of gas which converge at or near the point where the composition is extruded from the aperture; preferably the angle between the converging gas streams is from 30° to 60°. At least part of the water in the composition is removed by the gas stream, and the rate of removal may conveniently be controlled by mixing the gas with the water vapour, for example air at a relative humidity of greater than 80% may be used. The velocity of the gas stream may be varied over wide limits, but we prefer to use velocities in the region of 200 to 1500 feet per second. The pressure employed to extrude the composition through the apertures will depend on the viscosity of the composition and on the desired rate of extrusion. We find that pressures from 16 to 100 lb/sq. inch absolute are convenient for compositions having viscosities up to about 100 poise.

The fibres produced by the blowing process are generally of small diameter, typically from 0.5 to 5.0 microns, which is a very suitable diameter range for paper-

making techniques. The fibres are generally in discontinuous lengths and may have very high ratios of length to diameter, for example greater than 5000. The fibres may be collected as individual fibres or they may be collected in the form of a yarn, mat, blanket or felt. If they are collected as individual fibres they may be made into paper, board, blanket or felt, by any convenient method. If they are collected in the form of a mat they may be made into a yarn, and made up into cloth for use in the invention. Fibres having mean diameters from 1 to 3 microns are especially useful. Substantial freedom from shot, that is material of a non-fibrous nature in the fibre, is an advantage in producing papers and other structures according to the invention. Fibrising of aqueous solutions of metal compounds especially by blowing as hereinbefore described produces fibre, with a greatly reduced shot content compared with other methods for making refractory oxide fibres. Fibres having a specific surface area of 0.5 m²/g to 150 m²/g are preferred.

According to another aspect of the invention a precursor of a refractory structure comprises a paper, cloth, sheet, board, blanket or felt of refractory metal oxide fibres and a composition convertible to give a refractory bonding agent.

The compositions convertible to form a refractory bonding agent are preferably liquids containing compounds which can form a refractory oxide or an aluminium phosphate for example by heating. Among suitable compounds which can form refractory oxides are colloidal or dissolved inorganic oxy compounds, for example hydrated oxide sols of alumina, silica, titania, zirconia or mixtures thereof. Oxychlorides, basic acetates or basic formates of aluminium and/or zirconium are especially preferred. Alumino-silicates are also useful. Silica sols under the names "Syton" or the reference number N 1030 or N 1050 (Nalfloc Ltd.) and alumina or alumina monohydrate (boehmite) sols under the names "Baymal" or "Cera-sol" are very suitable. ("Syton" and "Baymal" are registered Trade Marks) Alkali-metal silicates, organic esters of inorganic acids such as alkyl silicates and alkyl titanates may be used. As compounds reactable to form aluminium phosphate may be mentioned those disclosed in UK Patent Specification No. 1 322 722.

Finely-divided solid filter materials such as clays, calcined clays and other mineral silicates may be present within the fibres or on the surface of the paper, cloth, sheet board or felt, for example to modify the rheological or refractory properties. Lightweight fillers, for example exfoliated mica, may also be present.

Depending on the relative properties of fibre, binding agent and other materials present, the structures may have gas permeability, density, strength, resilience and thermal conductivity lying within a wide range and therefore suitable for a wider range of duty than a refractory structure previously proposed. Convenient proportions of binding agent lie between 1 and 50% by weight of the refractory oxide fibre present.

The refractory structure prepared according to the invention may take many forms depending upon the particular use to which it is put. Thus sheets may be built up into thick wads by laminating or otherwise combining them, with or without the use of a refractory binder, which may be the same as or different from that used to bond the fibres.

In one form of the invention the structure is a flat sheet or laminated assembly of flat sheets. Such a structure is normally to be supported by an outer metal or refractory framework; for example a plurality of sheets may be supported side-by-side in order to provide parallel gas passages affording a low pressure drop yet effective contact with the gas by virtue of the open texture of the sheets.

In a second form of the invention the refractory structure comprises a ridged or embossed sheet. Such sheets may have plane surfaces between ridges or bosses, or the ridging and/or embossing may be over-all. Ridges may or may not be parallel or regular and there may be two or more sets of ridges intersecting one another. Ridges and bosses may both be present and either may be upward or downward or both from the general plane of the paper. This list of possibilities illustrates an advantage of the invention, namely that it makes it possible to produce a great variety of sheet-like refractory materials.

More particularly, the invention provides a laminated assembly of such sheets lying together. The nodes of the ridges and/or bosses of successive sheets may be in contact so as to produce passages through the assembly. The ridged or embossed sheets may alternate with flat sheets, an arrangement that avoids the need to ensure accurate coincidence of nodes and is especially suitable when the sheets are to be formed into a spiral roll.

As an alternative the invention provides an assembly in which a single long sheet ridged or embossed at a pitch that is broad on one long side and tapers to a narrow pitch on the other side, is wound in a helix so as to produce radial passages. This assembly may include a flat helix interleaved with the ridged or embossed helix. Such assemblies require the use of paper, cloth,

sheet board, blanket or felt of adequate stretchability in its wet state.

Assemblies of sheets according to the invention can have, for example, 1 to 400 passages per sq. inch. Advantageously low bulk densities, for example, 0.25 g/cc are possible.

In the assemblies, the ridged and/or embossed sheets may be bonded to each other or to flat sheets, but this is not essential, provided the sheets are supported at their ends. Bonding of the sheets to each other or to supporting end members can be by means of the same bonding material as is used for the mutual adhesion of the fibres in the sheets.

The refractory structures according to the invention are generally resilient and their active surface for contact with gases can be increased by perforation or forming with louvres by cutting. Some of the serious difficulties experienced in supporting ceramic matrices in metal containers do not occur, owing to the flexibility of structures according to the invention.

The refractory structures according to the invention are useful for many applications, for example heat and electrical insulation, filtration, chemical treatment, (especially of gases) and acoustic insulation.

In the field of heat insulation the structures are useful as sleeves or boards used as liners or risers for casting or ingot moulds. As such structures are frequently discarded after one use, they may contain organic modifiers, for example fibres such as polyester or viscose fibres, rubber latices, starches which may serve to improve low temperature resilience of the structures. Such organic modifiers will normally be destroyed in use as a result of the high temperatures involved.

The structures are useful in filtration processes in which high temperature resistance is required of the filter, for example in filtration of molten metal prior to casting, or the filtration of hot waste gases containing particulate matter.

The refractory structures are also useful as separators in batteries and as electrolytic cell diaphragms.

Refractory structures according to the invention are especially suitable for treating gas for the purpose of silencing them or effecting chemical reactions. Owing to their low-pressure drop and high geometric surface, they can be used with or without the addition of further catalytic material, as catalysts for treating waste gases to remove atmospheric contaminants such as nitrogen oxides, carbon monoxide, hydrocarbons, sulphur dioxide, hydrogen sulphide, ammonia and solvent vapours. The invention provides especially a process for catalytically treating internal combustion exhaust

without or with added oxygen.

In making precursors of refractory structures according to the invention refractory metal oxide fibres may be impregnated with a composition convertible to give a refractory bonding agent and the composition is then subjected to the necessary conversion to produce the refractory structure according to the invention.

As impregnation is usually carried after the fibres have been formed into the paper, cloth, sheet, board, blanket or felt it may be desirable to remove or decompose organic bonding agent added during paper-making or felting before applying the convertible composition, otherwise access of the composition to the fibres may be impaired.

The precursor of the refractory structure is preferably made from refractory metal oxide fibres, especially alumina or zirconia fibres, produced by the fibrising of aqueous compositions of compounds of the metal as hereinbefore described. Especially preferred are fibres made by the blowing process described hereinbefore, as fibres of a suitable diameter and free from shot are thereby obtained.

Conversion of the impregnating composition to a refractory bonding agent is most conveniently carried out by heating. The temperature of heating will depend upon the decomposition temperature(s) of the compound(s) in the composition. For oxychlorides and salts of organic acids of metal decomposable to a refractory oxide, temperatures in the range 400°C to 1500°C are convenient. Relatively low temperatures, for example 80°C to 200°C are suitable for converting the compounds described in UK Patent Specification No. 1 322 722 to aluminium phosphate. The structures may be further heated to sinter the refractory bonding agents, for example at temperatures of 1000°C to 2000°C.

The impregnated paper, cloth, sheet, board, blanket or felt can, while still wet, be subjected to mechanical treatments suitable for forming a desired shape, particularly squeezing, stretching, ridging or embossing and these can be carried out batchwise or in a continuous web by passage over or between suitably formed surfaces which may be rollers. The paper, cloth, sheet, board, blanket or felt may also conveniently be shaped, for example by ridging or embossing, before impregnation.

After impregnation the impregnating composition is preferably converted to a non-flowable condition by chemical treatment as follows.

For hydrated oxide sols, treatment with organic acids and/or ammonium salts, for example as described in UK Patent Specification No. 1 329 085 is convenient. Treat-

ment with a solution of alum, especially at a pH of 3 to 5, is preferred.

For alkal-metal silicates, treatment with acid is suitable. Such treatments are conveniently slow-acting, as when a compound that slowly liberates acid is mixed into the fibre and silicate; suitable compounds are silico fluorides and hydrolysable organic esters such as ethyl acetate. A convenient chemical treatment, though more rapid, is with carbon dioxide.

For esters of inorganic acids, hydrolysis is most convenient, particularly in the presence of a strong acid such as hydrochloric acid in a catalytic amount.

Normal or raised temperatures can be employed in the chemical treatment.

As an alternative to the chemical treatment the impregnated paper, cloth, sheet, board or felt may be partly dried, so as to leave it flexible, before the mechanical treatment. This drying should be preferably by some form of uniform heating such as dielectric, micro-wave or infra-red heating.

A retention aid, for example a cationic polymer such as polyacrylamide, may advantageously be added to the impregnating composition or to the fibres before or after impregnation. A suitable concentration of retention aid is 0.01 to 0.20% by weight.

When the refractory structure is to be used for chemical treatment of gases, the fibre or bonding agent may itself be an active material for assisting chemical reaction, for example if it is alumina or aluminosilicate. More often the active material is a separate component. Then such material can be a constituent of the fibres, having possibly been added to the liquid from which the fibres were originally spun or blown as disclosed in UK Patent Specifications Nos. 1 360 197, 1 360 198, 1 360 199 and 1 360 200. The active material can be added with the bonding composition or to the otherwise finished refractory structure, or at more than one stage in making the structure.

The active material can be any of those that have been proposed for gas treatment, for example, transition metals and their oxides, basic compounds of alkali-metals and alkaline earth metals, and combination of two or more of these.

As catalysts, metals and oxides from Groups Ib and VIII of the Mendeleeff Periodic Table published in "Chemical Elements and Their Compounds Vol 1 by Sidgwick and oxides from Groups Va, VIa and VIIa are especially useful. The active material may be directly on the surfaces of the refractory structure or may be on or in a surface layer of material of relatively high specific surface such as active alumina or alkaline earth oxide.

The invention is illustrated by, but not

limited to, the following Examples:

Example 1

A paper, having a basis weight of 200 g/sq metre, consisting of alumina fibre (prepared as described in Example 5* of UK Patent Specification No. 1 360 200) bonded with 10% of an acrylic latex, was impregnated with a colloidal solution of silica (N 1030 ex Nalflor Ltd). The impregnated paper was treated with a 0.5% w/v solution of alum followed by a 0.02% w/v solution of polyacrylamide ("Magnafloc" R 292 ex Allied Colloids Ltd). ("Magnafloc" is a registered Trade Mark. The paper was drained and placed on a corrugated former where it was dried to a uniform corrugated shape. The sheet was fired at 800°C to remove organic matter.

Example 2

An assembly was made consisting of a corrugated sheet of alumina fibre mounted on a flat sheet of alumina fibre and bonded thereto with an acrylic resin. This assembly was spirally rolled up to form a cylinder and impregnated with colloidal silica (N 1030 ex Nalflor Ltd). The impregnated cylinder was treated with 0.5% w/v alum solution followed by a 0.02 w/v solution of polyacrylamide (Magnafloc). The cylinder was dried at 100°C, then fired at 800°C to remove organic matter.

Example 3

A web of zirconia fibre prepared as described in Example 15* of UK Patent Specification No. 1 360 197 — was wound on a cylindrical former to form a tube and then impregnated with a 5% w/w solution of alumina sol. The impregnated tube was treated with a 0.5% w/v solution of alum followed by a 0.02% w/v solution of polyacrylamide ("Magnafloc") ("Magnafloc" is a registered Trade Mark). The tube was then removed from the former and fired at 1000°C.

Example 4

Alumina fibre paper 12" × 12" in size was impregnated with a 5% by weight solution of sodium silicate (Q 79 ex ICI Ltd) and dried at 100°C. The treated paper was further treated with 4N hydrochloric acid for ten minutes after which it was washed free of acid. The product was then fired at 800°C to give a refractory sheet suitable as a heat-insulating panel.

Example 5

Alumina fibre papers of thickness 0.040" were dipped into a sodium silicate solution of relatively low Na₂O:SiO₂ ratio in the range 1:2.5 - 1:4.0 Na₂O:SiO₂, the total solids content of the solution being 20%.

* As hereinafter described

Following lay-up of as many sheets as required to give a final thickness of 1/4 inch the stack was pressed in a mould at a pressure of 100 psi. Following removal from the mould the product was dried at 80-100°C for 24 hours when it had great strength. Improved stability to aqueous environments was achieved by firing at 800°-1000°C for 1/2 hour. Modulus of rupture values up to 4000 psi were obtained and the density was in the range 40-60 lb/ft³. The product was heat-resistant up to 1000°C, strong and abrasion-resistant, rendering it suitable for use as lightweight panels in fire doors, furnace linings and hot tops.

Example 6

A paper, having a basis weight of 100 g/sq metre, consisting of zirconia fibres (prepared as described in Example 3) and impregnated with 20% by weight of a fibrous alumina hydrate sol was passed, while still wet, between a mashing pair of corrugated rollers having a constant mesh separation of 0.040 inch. The rollers were heated at 120°C and a stream of air at 140°C was directed on to the paper as it emerged from the rollers. A corrugated paper was thus produced which was cut into sheets approximately 4 inch × 4 inch. Sheets of similarly impregnated and dried flat paper were also cut to approximately 4 inch × 4 inch. Fibrous alumina hydrate sol was deposited on the ridges of the corrugated sheets and a stacked assembly was made consisting of alternate corrugated and flat sheets. The assembly was dried at 100°C under light compression, fired at 700°C and cooled. It was then impregnated with 10% by weight of colloidal silica (N 1030 ex Nafloc Ltd). After drying at 100°C the assembly was fired at 1000°C to give a strong refractory structure.

Example 7

Corrugated zirconia fibre paper sheets were prepared as described in Example 6. A long flat 4 inch wide sheet of zirconia fibre paper of basis weight 100 g/sq metre was prepared. The zirconia fibre was prepared as described in Example 3 and the paper contained as binder 5% by weight of an acrylic resin and 5% by weight of micro-fine glass fibre. The flat sheet was folded a number of times back and forth on itself to form a pleated 4 inch × 4 inch square stack. A 4 inch × 4 inch sheet of corrugated paper was placed in each of the folds to form a honey comb-type box structure. The four closed sides of the structure were covered with a cement formed from zirconia fibre and alumina sol and the two open sides were sprayed with a colloidal silica sol. The structure was dried and then fired at 800°C.

The preparation of alumina and zirconia fibres as used in the Examples is described in UK Patent Specifications Nos. 1 360 197 and 1 360 200, Example 5 of Specification 1 360 200 in the case of alumina fibres and Example 15 of Specification 1 360 197 in the case of zirconia fibres. In Example 5 thereof 50 ml of aluminium oxychloride solution containing 11.2% by weight of Al and 8.1% by weight of Cl were mixed with 30 ml of a 2% by weight solution of a high molecular weight polyvinyl alcohol. The mixture was concentrated by evaporation under reduced pressure to a viscosity of 50 poise. The concentrated solution was introduced into a fibre-blowing device in which two high velocity streams of air impinged from either side at an angle of 30° to a stream of the solution emerging from a 25 micron wide aperture under pressure. The air streams were at a temperature of 35°C and a relative humidity of 40%.

A mat of very fine fibres having lengths up to 10 cm and diameters estimated to be 1 micron was collected on a gauze screen. The mat was heated as 800°C for 1 hour to give clear glassy fibres which were silky and flexible.

In Example 15 thereof a solution suitable for the production of a high-temperature resistant yttria-stabilised zirconia fibre, particularly useful for thermal insulation was prepared from:

500 g zirconium acetate solution (22% w/w ZrO₂),
220 cc 1% w/w polyethylene oxide solution,
12.8 g yttrium chloride hydrate,
2 cc concentrated hydrochloric acid.

The solution was reduced on a vacuum rotary evaporator to a viscosity of 15 poise at 20°C, and placed in a vessel fitted with a spinneret hole of diameter 0.001 inch.

A high velocity jet of air emerging through slits on either side of this hole and converging at an angle of 30° served to draw down a jet of liquid from the hole to essentially shot-free fibre with a mean diameter of 1.5 microns.

The fibres were dried at 200°C for 1/2 hour to give fibres with a mean diameter of 1 micron.

One preferred example of a refractory structure is shown in the drawings accompanying the provisional specification, in which

Fig. 1 shows isometrically a view of a complete matrix according to the invention; and

Fig. 2 shows isometrically a section along two planes of a detail of the matrix of Fig. 1.

The matrix consists of a sandwich of flat sheets 10 of thickness 0.01 inch thick alternating with embossed sheets 12 of the same

thickness. The embossing is overall, with-out flat areas, and with upward bosses alternating with downward bosses, at a pitch of 1 cm and an overall amplitude of about 2.5 mm. At the top and bottom of the sandwich lie thick sheets 14 of flat paper of thickness 0.03 inch. The sandwich is in slight compression between flanges 18 of side sheets 16. The ends of the thin sheets are cemented by alkali silicate layer 20 to side sheets 16, and layer 20 also cements sheets 14 to flanges 18 formed on side sheets 16.

15 WHAT WE CLAIM IS:—

1. A refractory structure comprising a paper, cloth, sheet, board, blanket or felt of refractory metal oxide fibres bonded with a refractory binding agent wherein the refractory metal oxide fibres are formed by fibrising a composition having a viscosity of greater than 1 poise comprising an aqueous solution or sol of a metal compound which can form a refractory oxide and a minor proportion of a water-soluble organic polymer, drying the fibre formed and heating to decompose the metal compound to oxide and to decompose the polymer.
2. A refractory structure as claimed in claim 1 wherein fibrising comprises extruding the fibrising composition through one or more apertures into at least one gas stream having a component of high velocity in the direction of travel of the extruded composition.
3. A refractory structure as claimed in claim 2 wherein the gas streams converge at or near the point where the composition is extruded from the aperture.
4. A refractory structure as claimed in claim 2 or 3 wherein the gas is mixed with water vapour.
5. A refractory structure as claimed in claim 4 wherein the gas is air at a relative humidity of greater than 80%.
6. A refractory structure as claimed in any one of claims 1 to 5 wherein the metal compound is an oxychloride, basic acetate, basic formate or nitrate of aluminium and/or zirconium and which is decomposed to alumina and/or zirconia.
7. A refractory structure as claimed in any one of claims 1 to 6 wherein the water-soluble organic polymer is polyethylene oxide, polyvinyl alcohol or polyvinyl pyrrolidone.
8. A refractory structure as claimed in any one of claims 1 to 7 wherein the refractory metal oxide fibre has a diameter from 0.5 to 5.0 microns.
9. A refractory structure as claimed in any one of claims 1 to 8 in the form of a flat sheet or in the form of a laminated assembly of flat sheets.
10. A refractory structure as claimed in any one of claims 1 to 8 in the form of a ridged or embossed sheet or in the form of a laminated assembly of ridged or embossed sheets.
11. A refractory structure as claimed in any one of claims 1 to 8 in the form of a laminated assembly of flat sheets and ridged or embossed sheets.
12. A refractory structure as claimed in claim 11 wherein flat sheets alternate with ridged or embossed sheets.
13. A refractory structure as claimed in any one of claims 9 to 12 wherein the sheets are in the form of a spiral roll.
14. A refractory structure as claimed in any one of claims 9 to 13 wherein sheets are bonded together within an assembly.
15. A refractory structure as claimed in claim 14 wherein the sheets are bonded by the same refractory binding agent as that used to bond the fibres in the sheet.
16. A refractory structure as claimed in any one of claims 1 to 15 which comprises or contains a catalytic material for treating waste gases.
17. A precursor of a refractory structure as claimed in any one of claims 1 to 16 comprising a paper, cloth, sheet, board, blanket or felt of refractory metal oxide fibres and a composition convertible to give a refractory bonding agent.
18. A precursor of a refractory structure as claimed in claim 17 wherein the composition convertible to give a refractory bonding agent is a liquid containing components which can form a refractory oxide or an aluminium phosphate on heating.
19. A precursor of a refractory structure as claimed in claim 18 wherein the liquid contains a colloidal or dissolved inorganic oxy compound.
20. A precursor of a refractory structure as claimed in claim 19 wherein the colloidal oxy compound is a sol of alumina, silica, titania, zirconia or mixtures thereof.
21. A precursor of a refractory structure as claimed in claim 19 wherein the oxy compound is an oxychloride, basic acetate or basic formate of aluminium and/or zirconium.
22. A method of making a precursor of a refractory structure as claimed in any one of claims 17 to 21 comprising the step of impregnating refractory oxide fibres with a liquid composition convertible to give a refractory bonding agent.
23. A method as claimed in claim 22 wherein the refractory metal oxide fibres are formed by fibrising a composition having a viscosity of greater than 1 poise comprising an aqueous solution or sol of a metal compound which can form a refractory oxide and a minor proportion of a water-soluble organic polymer, drying the

fibre formed and heating to decompose the metal compound to oxide and to decompose the polymer.

24. A method as claimed in claim 22 or 23 wherein the refractory oxide fibres are in the form of a paper, cloth, sheet, board, blanket or felt.

25. A method as claimed in any one of claims 22 to 24 wherein the impregating composition is converted to a non-flowable condition.

26. A method as claimed in claim 25 wherein conversion of the composition to a non-flowable condition is carried out by chemical treatment or by partial drying.

27. A method as claimed in any one of claims 22 to 26 wherein the paper, cloth, sheet, board, blanket or felt is subjected to mechanical treatment suitable for forming a desired shape before or after impregnation.

28. A method as claimed in claim 27 wherein the mechanical treatment is one of squeezing, stretching, ridging or embossing.

29. A method as claimed in any one of claims 22 to 28 wherein a catalyst material or precursor thereof for treating waste gases is included in the liquid bonding composition, in the composition from which the

fibres are made or added to any constituent part of the refractory structure.

30. A method of making a refractory structure as claimed in any one of claims 1 to 16 comprising heating a precursor of a refractory structure as claimed in any one of claims 17 to 21.

31. A method as claimed in claim 31 wherein the precursor is heated at a temperature of 400°C to 1500°C.

32. A refractory structure substantially as described and as illustrated in the drawing.

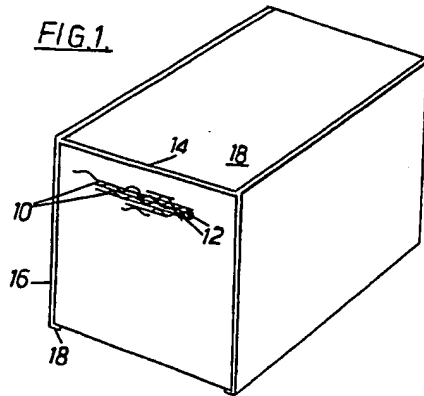
33. A refractory structure or a precursor thereof substantially as described with reference to Examples 1 to 5.

34. A refractory structure or a precursor thereof substantially as described with reference to Examples 6 and 7.

35. A method of making a refractory structure or a precursor thereof substantially as described with reference to Examples 1-5.

36. A method of making a refractory structure or a precursor thereof substantially as described with reference to Examples 6 and 7.

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FIG.1.FIG.2.